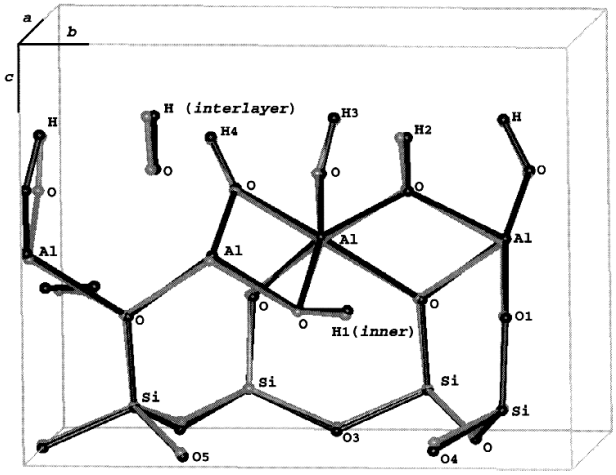
RESEARCH HIGHLIGHT
Office of Basic Energy Sciences
Geosciences Program

Project: Heterogeneous Nucleation and Growth Kinetics of Clays

Who and Where: Randall T. Cygan, Kathryn L. Nagy, and J. David Hobbs; Geochemistry Department, Sandia National Laboratories, Albuquerque, NM 87185-0750

Objective: Clay nucleation and growth often occur heterogeneously and/or epitaxially on detrital minerals. Kinetics of these processes and role of nucleating substrates are unknown. The goal of the project is to quantify and model clay mineral growth by examining the reaction at the surface, to assess reactive surface area, and to provide kinetic data for accurate modeling of weathering and diagenesis.



Results: A key element in the atomistic modeling of the growth mechanisms of clay minerals is having a theoretical basis for the bulk crystal structure of the clay. In this effort we have obtained an energy-minimized and optimized structure of kaolinite ($Al_2Si_2O_5(OH)_4$) using a first-principles quantum approach based on local density functional theory. The high-level basis set calculations were performed on two proposed crystal structures derived from two different refinements of low temperature neutron diffraction data. A steepest gradient method was used to fully optimize all 34 atoms of the kaolinite unit cell. The resulting structure is in excellent agreement with the Bish (1993) refinement (see figure with overlay of structures; theoretical model is in black), and confirms the existence of a kaolinite unit cell having C1 symmetry. The results indicate the influence of the octahedral vacancy in controlling the inner hydrogen atom position.

Significance: The results of this work provide the first *ab initio* determination of the structure of a clay mineral. This achievement is obtainable primarily due to the use of a massively parallel supercomputer, where previously such attempts were prohibitive in cost requiring months of computational time rather than days as demonstrated here. This research demonstrates that researchers can determine crystal structures of clays and related cryptocrystalline materials for which suitably-sized single crystals, required for X-ray diffraction refinements, are lacking.

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